

Perovskite Based Catalysts for Diesel Reforming in Solid Oxide Fuel Cell Application

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Fuel reforming represents a key technology challenge for diesel-based solid oxide fuel cell (SOFC) power plants. Among conventional hydrocarbon fuels, diesel has the highest energy density and hydrogen content per unit volume, which is an ideal source for the production of hydrogen-rich reformate. On the other hand, commercial diesel also contains high levels of organic sulfur and heavy aromatics; both are known to impede catalytic reforming reaction and deactivate the catalyst.

At Argonne National Laboratory, we have been focusing on developing technology solutions for a commercially viable diesel reformer. One of our focus areas is a low-cost diesel reforming catalyst. We conducted an extensive investigation of perovskite-based materials as a potential low-cost alternative for autothermal reforming (ATR). Transition-metal perovskites have the key attributes for a robust reforming catalyst. Since the metals are embedded in the oxide framework with high crystallinity, most perovskites are stable under both oxidizing and reducing environments at elevated temperatures. Both the A and the B site in a perovskite can be partially substituted by different types of cations, A' and B'; it is therefore relatively easy to alter the formulation from ABO_3 to $\text{A}_{1-x}\text{A}'_x\text{B}_{1-y}\text{B}'_y\text{O}_{3-e}$ while maintaining a stable crystal structure. This enables us not only to create an effective catalyst through reformulating the composition by properly incorporating the transition metals with synergetic POX or SR activities, but also to generate new active sites through material synthesis with designed charge deficiency and lattice distortion. In our laboratory, we have synthesized nearly 30 different formulations of transition-metal perovskites through a glycine/nitrate self-combustion process, with ruthenium-doped chromite, aluminite and ferrite as the most effective ones. The catalytic reforming activities were tested in a plug-flow reactor using surrogate diesel or JP-8 under various pre-defined oxygen-to-carbon ratios and steam-to-carbon ratios at a typical space velocity $>100,000 \text{ hr}^{-1}$. The reforming efficiency to form H_2 and CO, as well as the selectivity of COx formation, was measured under these experimental conditions. We also conducted a series of short-term (200 hour) and mid-term (1000 hour) aging tests using sulfur-containing surrogate fuel and pre-blended gas mixture and found that our catalysts maintained relatively stable catalyst activities throughout the test. Through our study on reforming chemistry of individual and blended diesel components, we found strong temporary deactivation effect by the polyaromatics on the overall reforming reaction rate. Mechanistic explanation and potential solution will be discussed.

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